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Vibrational spectra of isomeric aminobenzonitriles

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Vibrational spectra of benzonitrile, its mono- and di-substituted derivatives have been studied by various workers (Jacobson 1965, Green and Harrison 1976, Joshi *et al* 1987, Aquil and Verma 1982, Rastogi *et al* 1990, 1991). Inspite of a large amount of spectral data available for these molecules, difference in the interpretation of the spectra are still considerable. As the complete vibrational data for three isomeric aminobenzonitriles is not available in literature, we undertook the study of the vibrational spectra of *o*-, *m*- and *p*-aminobenzonitriles.

The spectrally pure samples of *o*-, *m*- and *p*-aminobenzonitriles, hereafter referred to as OAB, MAB and PAB were obtained from M/S Aldrich Chemical Co, USA and used as such without further purification. The Raman spectra of *m*- and *p*-aminobenzonitriles in the solid phase were recorded on a Spex Laser Raman Spectrophotometer (Ramalog) using, for excitation, 514.5 nm of radiation from a 2W Argon ion laser from Spectra Physics. Spectral slit width was 10 cm^{-1} in both the cases but the laser powers were varied from 100 mW to 300 mW depending upon the scattering property of the sample concerned. The detection was made by a thermoelectrically cooled PM tube (HAMMATSU R 995P) operated on PC mode. The compound *o*-aminobenzonitrile is too fluorescent and it was impossible to record its Raman spectra. The IR spectra were recorded on a Perkin-Elmer 577 grating spectrophotometer and Nicolet DX IR spectrophotometer in the 200-4000 cm^{-1} (except for PAB in KBr and nujolmull matrices in which case spectra were recorded in 650-4000 cm^{-1}) region.

Figure 1 shows the structures of benzonitrile and *o*-, *m*- and *p*- aminobenzonitrile molecules with classical numbering of the atoms. From the structural point of view the compounds OAB and MAB belong to the point group C_s, while PAB to the C_{2v} point group. The 39 normal modes of vibrations will be distributed over the possible species $27a' + 12a''$ in compounds OAB and MAB and $14a_1 + 4a_2 + 13b_2 + 8b_1$ in PAB. The analysis of the bands and the assignment of the

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fundamental frequencies are made on the basis of magnitude and relative intensities of the observed bands and help has been taken from the assignments made by earlier workers in the related molecules. The wavenumbers of the observed fundamental bands in IR and Raman spectra alongwith the proposed assignments are given in Table 1.

Skeleton vibrations :

The appearance of a group of four bands in the region 1350-1620 cm^{-1} in the spectra of substituted benzenes represent the two doubly degenerate C–C stretching modes namely, e_{2g} (1595 cm^{-1}) and e_{1u} (1485 cm^{-1}). It is usually observed that

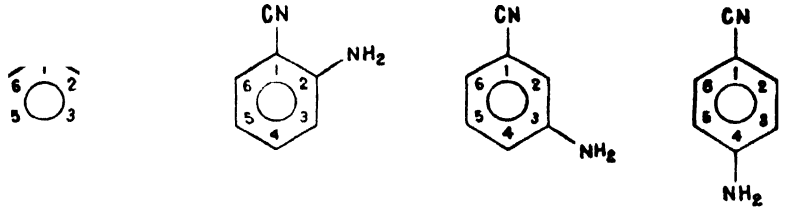

Figure 1. Structures of (1) benzonitrile, (2) *o*-, (3) *m*-, and (4) *p*-benzonitriles.

one of the two components of these two frequencies is lowered while the other component retains the energy of the degenerate vibration in benzene. On the basis of this criterion the bands observed at 1592 and 1580 cm^{-1} in OAB, 1606 and 1578 cm^{-1} in MAB and at 1599 and 1520 cm^{-1} in PAB have been assigned as the two components of the e_{2g} vibration of benzene. Similarly the pairs of frequencies 1496 and 1460 cm^{-1} in OAB, 1515 and 1438 cm^{-1} in MAB and 1470 and 1388 cm^{-1} in PAB have been assigned as two components of the e_{1u} (1485 cm^{-1}) mode of vibration of benzene.

As pointed out by several workers the C–C ring breathing a_{1g} (995 cm^{-1}) and C–C–C trigonal bending b_{1u} (1010 cm^{-1}) vibrations of benzene give rise to combined modes in molecules belonging to the reduced symmetry. As a result of this, one of the modified modes is considerably reduced and lies between 700-900 cm^{-1} depending upon the mass and nature of substituent, while the other keeps itself around 1000 cm^{-1}. These two vibrations have been identified at 1020 and 860 cm^{-1} in OAB, 1008 and 827 cm^{-1} in MAB and at 1016 and 819 cm^{-1} in PAB. Corresponding to the other planar carbon bending vibration e_{2g} (608 cm^{-1}) of benzene, there occurs two vibrations in substituted benzenes, one of which with considerably reduced frequency. These two vibrations have been observed at 582 and 498 cm^{-1} in OAB and at 574 and 463 cm^{-1} in MAB. In the case of PAB, only one vibration could be identified at 475 cm^{-1} in IR and at 490 cm^{-1} in Raman spectrum, while the other vibration could be observed neither in IR nor in Raman spectra.

It has been reported in literature (Varsanyi 1969, 1974) that in all primary aromatic amines, a strong band appears in the region 1250-1360 cm^{-1} and the

Table I. Assignment of vibrational frequencies (in cm^{-1}) of isomeric aminobenzonitriles.

Compound											
OAB (C_s) Sym. species	IR KBr	IR Nujol	MAB (C_s) IR / CsI	Raman	PAB (C_{2v}) Sym. species	IR KBr	IR Nujol	IR CsI	Raman	Vib. No.	Assignment
a'	3462 vs	3460 s	3484 vs	—	a_1	3490 w	3460 m	—	—	—	NH_2 asym. stretch
a'	3369 vs	3367 s	3375 vs	—	b_2	3370 w	3395 s	3340 s	—	—	NH_2 sym. stretch
—	3238 s	—	—	—	—	—	—	—	—	—	ν (N–H) } associated
—	3228 s	—	3218 s	—	—	—	—	3205 s	—	—	ν (N–H) } associated
a'	—	—	3120 vw	—	a_1	—	3120 vw	—	—	20*b*	ν (C–H)
a'	3080 s	—	3070 w	—	a_1	—	—	—	—	2	ν (C–H)
a'	3045 s	—	3058 sh	—	b_2	—	—	3048 vw	—	20*a*	ν (C–H)
a'	2236 vs	2236 m	2210 vvs	2232 s	a_1	2220 vs	2235 vs	2197 vs	2210 vvs	—	ν (C≡N)
a'	1634 vvs	1634 s	1628 vvs	—	b_2	1630 sh	1640 sh	—	1628 w	—	NH_2 scissor
a'	—	1592 m	1604 vvs	1606 m	b_2	1610 vvs	1617 vs	1595 vs	1599 vs	8*b*	ν (C–C)
a'	1568 vvs	1580 m	1570 sh	1578 w	a_1	1515 vs	1510 w	1516 m	1520 w	8*a*	ν (C–C)
a'	1496 vvs	1496 sh	1515 vs	—	a_1	—	1470 vs	1500 m	—	19*b*	ν (C–C)
a'	1460 vvs	1466 vvs	1438 w	—	b_2	—	1388 vs	—	—	19*a*	ν (C–C)
a'	1346 s	1358 m	1332 sh	—	b_2	—	—	—	1340 vw	7*b*	ν ($C-NH_2$)

Table I. (Contd.)

Compound											
OAB (C_s) Sym. species	IR		MAB (C_s) IR	Raman	PAB (C_{2v}) Sym. species	IR			Raman	Vib. No.	Assignment
	KBr	Nujol	CsI			KBr	Nujol	CsI			
a'	1316 vs	1328 s	1317 vs	1326 w	b_2	1322 vs	1320 vs	1319 vvs	1314 vw	14	ν (C–C)
a'	1268 vvs	1280s	1300 sh	1295 m	b_2	—	—	—	—	3	β (C–H)
a'	1226 s	1220 m	—	—	a_1	1220 m	1222 m	1217 m	1220 m	9a	β (C–H)
a'	1208 s	1202 sh	1210 m	—	b_2	—	—	—	1196 vw	9b	β (C–H)
a'	1172 s	1172 s	1175 vvs	1169 vw	a_1	1182 vs	1184 vs	1177 vs	1173 vs	13	ν (C–CN)
a'	1154 s	1136 s	1136 m	—	b_2	1145 s	1148 s	1140 s	1138 w	15	β (C–H)
a''	1068 m	1064 m	—	—	b_1	1076 vw	—	—	—	—	NH_2 twisting
a'	1020 m	1012 w	1008 w	991 s	a_1	1016 m	—	1012 m	—	12	ϕ (C–C–C)
a''	968 m	960 w	966 w	—	b_1	978 m	980 m	970 m	976 vw	5	γ (C–H)
a''	912 w	906 w	943 w	935 w	b_1	957 m	—	948 m	—	17b	γ (C–H)
a''	878 m	874 sh	835 vs	—	a_2	845 vs	846 vs	832 vvs	842 s	10a	γ (C–H)
a'	860 s	858 w	827 s	795 vw	a_1	—	—	—	819 sh	1	ν (C–C) (ring breath)
a''	750 vvs	750 s	—	738 sh	b_1	734 w	732 vw	742 w	—	10b	γ (C–H)

Table I. (Contd.)

Compound											
OAB (C_s) Sym. species	IR KBr	IR Nujol	MAB (C_s) IR / CsI	Raman	PAB (C_{2v}) Sym. species	IR KBr	IR Nujol	IR CsI	Raman	Vib. No.	Assignment
a''	738 sh	730 sh	712 w	720 m	b_1	715 s	706 m	717 w	702 w	4	δ (C–C–C)
a'	—	620 w	693 s	—	a_1	684 vw	680 w	682 vs	651 m	—	NH_2 wagging
a'	582 m	576 vw	—	574 vw	b_2	—	—	—	—	6*b*	ϕ (C–C–C)
a'	564 m	561 vw	538 vs	534 w	b_2	—	—	535 vs	—	—	β (C≡N)
a'	498 vvs	498 m	470 w	463 w	a_1	—	—	475 vw	490 vw	6*a*	ϕ (C–C–C)
a''	410 vs	—	—	—	a_2	—	—	—	420 w	16*a*	δ (C–C–C)
a'	380 s	—	380 m	393 w	a_1	—	—	372 sh	389 vw	18*a*	β (C–NH_2)
a'	278 sh	278 vvs	336 m	—	b_2	—	—	330 vs	—	18*b*	β (C–CN)
a''	246 sh	242 vvs	—	245 vw	b_1	—	—	250 sh	265 vw	—	γ (C≡N)
a''	233 sh	230 vvs	—	—	a_2	—	—	—	240 sh	17*a*	γ (C–NH_2)
a''	222 vs	224 s	—	—	b_1	—	—	230 sh	—	11	γ (C–CN)
a''	212 vvs	215 s	—	—	a_2	—	—	—	—	—	NH_2 torsion
a''	—	—	—	170 s	b_1	—	—	—	170 w	16*b*	δ (C–C–C)

v=very, s=strong, w=weak, m=medium, sh=shoulder, β and ϕ=in-plane bending, γ and δ=out-of-plane bending, asym=asymmetric, sym=symmetric.

intensity of this band appears to be variable and probably it is associated with substituent and has been assigned to C–NH_2 stretching vibration. Goel *et al* (1978) have assigned the strong bands observed at 1312 and 1302 cm^{-1} in 2,3- and 3,5-dichloro anilines respectively to this mode of vibration. In the present case the bands observed at 1346, 1332 and 1340 cm^{-1} in OAB, MAB and PAB respectively have been assigned to the C–NH_2 stretching vibration.

Green (1961) and Jacobson (1965) have assigned a band at 1192 cm^{-1} to the C–CN stretching mode. The strong bands observed at 1172, 1175 and 1182 cm^{-1} in the IR spectra of OAB, MAB and PAB respectively have been assigned to this mode in accordance with the assignments proposed by Singh (1969) in *o*- and *m*-fluoro benzonitriles and by Sinha and Chatterjee (1976a, 1976b) in *m*- and *p*-methyl benzonitriles respectively. In Raman spectra also a strong band at 1173 cm^{-1} in PAB and a weak band at 1169 cm^{-1} in MAB has been observed corresponding to this mode of vibration.

CN group vibrations :

Saito *et al* (1981) have suggested that a band at 2223 cm^{-1} (a calculated value) in benzonitrile is highly localised at a C–C≡N part and is the band characteristic of the C≡N stretching vibration. They have also shown by a study on several *m*- and *p*-benzonitriles that the position of this band is not affected much by the kind of substituents. In the present study, the strong band at 2236 cm^{-1}, 2232 cm^{-1}, 2210 cm^{-1} in the three molecules respectively have been assigned to this mode of vibration. The bands observed at 564, 538 and 535 cm^{-1} have been assigned to the in-plane C≡N deformation mode in accordance with the assignments proposed by Kuwae and Machida (1979) for deuterated benzonitriles. The C≡N out-of-plane bending vibrations have been identified at 246, 245 and 250 cm^{-1} respectively in these molecules.

NH_2 group vibrations :

The NH_2 group involves the symmetric and asymmetric N–H stretching vibrations. In the case of nearly all the primary aromatic amines, two bands (Bell 1962, Ellis 1928) occur in the region 3300-3500 cm^{-1}. The bands around 3500 cm^{-1} have been assigned by a large number of workers as asymmetric and that appearing around 3400 cm^{-1} as symmetric stretching vibration. Both of these are subject to small changes with alteration of polarity of the solvent and to rather large changes in concentrated solutions in which intermolecular association can occur. Intramolecular bonding also lowers these frequencies. In view of these considerations, the strong IR bands observed at 3462 and 3369 cm^{-1} in OAB, 3484 and 3375 cm^{-1} in MAB and at 3490 and 3370 cm^{-1} in PAB have been assigned to the N–H (NH_2) asymmetric and symmetric stretching vibrations respectively. It has been pointed out by Bellamy (1959) that in N-octamide in $CHCl_3$ solution, the NH_2 free absorption occurs at 3530 and 3415 cm^{-1}, but it also shows additional bands at 3498,

3345, 3300 and 3182 cm^{-1}, suggesting different types of simultaneous association of free and bonded NH bonds. Therefore, the additional bands observed at 3228 and 3238 cm^{-1} in the IR spectra of OAB may be assigned to such NH_2 bonded absorption. Only one band at 3218 cm^{-1} in MAB and at 3205 cm^{-1} in PAB could be observed corresponding to such NH_2 bonded stretching vibration.

The NH_2 scissoring frequeucy has been suggested to lie in the region 1590-1650 cm^{-1} in nearly all primary aromatic amines (Rao 1963). The bands observed at 1634, 1628 and 1628 cm^{-1} in OAB, MAB and PAB respectively have been assigned to this mode, which find support from literature values in the case of various substituted anilines (Singh et *al* 1966).

The NH_2 wagging vibration is analogous to the inversion mode of ammonia (Albert and Nelson 1945). The infrared band corresponding to inversion mode of ammonia is observed at 950 cm^{-1} (mean of two bands). In methyl ammine (Cleaves and Phyler 1939), this bands is located at 783 cm^{-1} and in aniline at 660 cm^{-1}. In the present investigation this vibration is observed at 620, 693 and 682 cm^{-1} in OAB, MAB and PAB respectively. Sharma and Dwivedi (1976) and Ansari and Verma (1978) have also reported the NH_2 wagging vibration in this frequency range.

The assignments of the other vibrations in the compounds studied are presented in Table 1.

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